



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 21/10, 23/62, 23/58, C07C 5/333	A1	(11) International Publication Number: WO 99/46039 (43) International Publication Date: 16 September 1999 (16.09.99)
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(54) Title: IMPROVED CATALYST SUPPORT MATERIAL (57) Abstract <p>The present invention relates to a new catalyst support material comprising a mixed oxide essentially of a divalent metal and a trivalent metal in a substantially homogeneous phase, which is a calcination product of a hydrotalcite-like phase calcinated at a temperature of about 700 – 1200 °C, wherein the divalent metal/trivalent metal molar ratio is equal to, or higher than 2. The invention relates also to a process of preparing said support, a catalyst of dehydrogenation comprising a 1. Transition row metal and/or Group VIII metal impregnated on said support, and a process for dehydrogenation of light alkanes using said catalyst.</p>		

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Improved catalyst support material

Field of the invention

The present invention relates to the preparation of highly stable, high surface area catalyst carrier materials derived from hydrotalcite-type materials by calcination at an elevated temperature.

Background of the Invention

Hydrotalcite is a layered mineral of formula: $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. Over the years, a large number of hydrotalcite-like compounds, of general formula: $[\text{M(II)}_x\text{M(III)}_y(\text{OH})_{2z}]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where A = anions, have been prepared (1). These compounds are characterised by a sheet-like structure, in which the anions are located in the interlayer between two brucite-like sheets containing the metal ions. M^{II} , M^{III} metal ions having an ionic radius which is not too different from Mg^{2+} can form hydrotalcite-like compounds (1).

Upon calcination at 400-700°C, a high surface area (typically 160-220 m²/g) material with an XRD pattern typical for MgO is formed, without separation of the two metal ions into separate oxide phases (2). Upon calcination at even higher temperatures, the mixed oxide is gradually transformed into a spinel structure, i.e.; $\text{M}^{\text{II}}\text{M}^{\text{III}}_2\text{O}_4$, with a much lower surface area (3-4).

A catalyst comprising a Group VIII noble metal, a Group IVA metal, optionally a Group IA metal and a carrier substantially consisting of a mixed Magnesium/Aluminium Oxide Mg(Al)O is disclosed in Den norske stats oljeselskap's International Patent Application WO 94/29021. The catalyst is particularly suitable for the dehydrogenation of C_{2-5} alkanes to C_{2-5} alkenes with or without simultaneous oxidation of the hydrogen formed.

One major use for the materials described in the present application is as support materials for catalysts (1), for instance for the catalytic dehydrogenation of lower alkanes (5).

It has been reported that certain materials formed by calcination of a Mg-Al-containing hydrotalcite at 300-700°C exhibit a high stability towards sintering in a humid atmosphere (2)(6). In the present invention, it has been found that the materials covered by this invention predominantly maintain the MgO structure, and also a high specific surface area, after calcination at temperatures above 700°C. Further, it has been found that the materials thus formed exhibit an improved stability towards sintering compared to the materials reported in (2) and (6).

The International Patent Application WO94/29021 discloses a new catalyst and processes for dehydrogenating saturated hydrocarbons. The catalyst disclosed therein contains 0.1 to 1.0 percent by weight of a Group VIII noble metal, 0.1 to 3.0 percent by weight of a Group IVA metal, 0-0.7 percent by weight of a Group IA metal, calculated on the total weight of the catalyst. Said catalyst is prepared by incorporating a Group VIII noble metal, a Group IVA metal and optionally Group IA alkali metal onto a carrier consisting essentially of a mixed oxide of magnesium and aluminum, Mg(Al)O, and subjecting the thereby obtained material to a pretreatment (ROR pretreatment) comprising a reduction, preferably in hydrogen, subsequent oxidation, preferably in air optionally mixed with nitrogen, and finally a second reduction, preferably in hydrogen. The catalyst is described to be used in a process for dehydrogenating dehydrogenatable C₂₋₃₀ hydrocarbons, preferably C₂₋₅ paraffins, wherein the hydrocarbons under suitable dehydrogenation conditions are contacted in one or more reaction zones with a solid catalyst of the abovementioned composition.

The carrier for the catalyst may be prepared by adding a solution of sodium hydroxide and sodium carbonate to a solution of magnesium nitrate and aluminum nitrate according to the method described in Journal of Catalysis 94 (1985), the pages 547-557. Instead of sodium hydroxide and sodium carbonate, potassium hydroxide and potassium carbonate can be used, see Applied Catalysis 55

(1989) pages 79-90. A hydrotalcite-like compound $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ is formed by evaporation (drying) of the abovementioned mixtures. The hydrotalcite is then calcinated at a temperature 500-800°C to give $\text{Mg}(\text{Al})\text{O}$. The molar ratio of Mg to Al typically ranges from 1:1 to 10:1, and the surface area is typically ranging from 100 to 300 m^2 per gram, preferably from 140 to 210 m^2 per gram, and the particle size can be in the range of 100 μm to 20 μm .

Albeit a calcination temperature range of about 500 to about 800°C is indicated, the calcination temperature in the examples is consistently 700°C for about 15 hours.

Results of a dehydrogenation of propane is presented in Table 1 indicating an improved efficiency of the catalyst compared to prior art catalysts.

However, the inventors of the present invention have found that the stability of the catalyst prepared in WO94/29021 is still lower than desirable.

The aim of the present invention was therefore to develop a catalyst having the same catalytic performance as this prior art catalyst with regard to catalyst activity, but at the same time increasing the catalyst life time by preventing irreversible deactivation like sintering of the support.

Thus the present invention provides for a catalyst support material comprising a mixed oxide consisting essentially of a divalent metal and a trivalent metal in a substantially homogeneous phase, which is a calcination product of a hydrotalcite-like phase calcinated at a temperature of about 700 - 1200 °C, wherein the divalent metal/trivalent metal molar ratio is equal to, or higher than 2.

Tests of the effect of the calcination temperature of hydrotalcite and hydrotalcite-like materials at different temperatures from 700 °C to 1200 °C were therefore investigated.

By performing these investigations it was surprisingly found that by raising the calcination temperature of the catalyst support precursor hydrotalcite to the range of 750 to 950°C an improvement of the catalyst stability could be achieved with an

acceptable reduction in the surface of the catalyst carrier compared to the gain in stability at use. In a further aspect the present invention thus relates to a catalyst support material comprising a mixed oxide consisting essentially of Mg and Al in a substantially homogenous phase, which is a calcination product of a hydrotalcite phase, preferably calcinated at a temperature of 750 to 950°C, wherein the Mg/Al molar ratio is equal 2 or higher than 2. Particularly the calcination has been effected at 770 to 850 °C and preferred at about 800 °C .

Preferably the Mg/Al molar ratio is in the range of about 2.5 to 6.0, and particularly the Mg/Al molar ratio is in the range about 3 to about 5.

In another aspect of the present invention a method for preparing said catalyst support material is provided wherein a solution comprising a divalent metal salt and trivalent metal salt is mixed with a basic aqueous solution, the reaction product recovered from said reaction mixture, said product being washed and dried, and the dried product is calcinated at a temperature ranging from about 700 - 1200 °C.

The preferred divalent metal therein is Mg and the preferred trivalent metal therein is Al.

Calcination temperatures in the range of 750 - 950 °C have been found particularly suitable.

More preferably the calcination takes place at a temperature ranging from about 770 to about 850°C.

The best results have so far been achieved when the calcination was performed at about 800 °C .

The calcination may be effected for f.i. about 1 to about 20 hours, and preferably the calcination is effected for about 2-15 hours.

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The basic aqueous solution used in this process is preferably a composition of aqueous ammonium or alkali metal hydroxides and carbonates.
—

The molar ratio of hydroxide to carbonate may f.i. be within the range of 1:1 to 3:1.

In another aspect the present invention relates to a dehydrogenation catalyst comprising a 1. Transition row metal of the Periodic System and/or a Group VIII metal impregnated on to the catalyst support described above.

Preferably the 1. Transition row metal of the Periodic System is Cr.

Preferably this catalyst comprises both a Group IVA metal and a Group VIII metal impregnated on to the catalyst support material mentioned above. Optionally a Group IA metal may be used together with the Group VIII metal and the Group IVA metal.

Preferably the Group VIII is Pt, the Group IV metal is Sn and the Group IA metal is Cs. Preferably the Group VIII metal catalyst is in the range of 0.05 to 5.0 percent by weight and the amount of the Group IVA metal is 0.05 to 7.0 percent by weight, optionally Group IA 0,05 to 5 percent by weight.

The present invention also relates to a process for the catalytic dehydrogenation of light alkanes wherein a stream of such light alkanes is passed through a layer of the catalytic active compositions described above in the presence or absence of steam.

Thus, according to one embodiment this process is performed in the presence of steam.

In another embodiment the process is performed in the absence of steam.

At last the present invention relates to the use of the catalytic composition as described above for the dehydrogenation of light alkanes.

Figures:

Figure 1 shows steam stabilisation tests at 650 °C, materials prepared by Mg/Al ratio 3 and 5 and calcination temperature 700 and 800 °C.

Figure 2 shows steam stabilisation tests at 650 °C , materials prepared by Mg/Al ratio 3 and 5 and calcination temperature 800 °C .

Figure 3 shows steam stabilisation tests at 650 °C , materials prepared by Mg/Al =3 and calcination temperature 700 °C by using NH_4^+ or Na^+ salts in the precipitation of the materials.

Figure 4 shows steam stabilisation test and thermic stabilisation test at 650 °C , materials prepared by Mg/Al =5 and calcination temperature 800 °C .

The steam testing discussed later in the following examples shows that materials calcinated at 800°C after 72 hours have a higher specific surface area than those calcinated at 700°C. (See fig. 1.)

This involves a less frequent change of catalyst in the dehydrogenation process of light alkanes to alkenes. This less frequent changing of catalyst is of great importance when running a dehydrogenation reaction in industrial plants. This surprising improvement was not to be expected from the prior art disclosure as set forth in the International Application WO94/29021 discussed above.

The following Examples are set forth to illustrate the invention disclosed herein. These examples should not, however, be construed as limiting the scope of the novel invention:

General

Calcination was performed under flowing air (100 ml/min). The sample (5-50 g) was heated with a heating rate of 3°C/min to the final calcination temperature. After completing the calcination, the sample was cooled with a cooling rate of appx. 2°C/min.

Specific surface area was measured using nitrogen by the BET method. The measurement accuracy was $\pm 5\%$. Powder XRD (Siemens D-5000 diffractometer with Cu-K_α radiation) was used to check crystallinity.

Example 1

A Mg(Al)O material having an atomic ratio of Mg to Al of 3:1 was prepared according to the following procedure: An aqueous solution of 0.55 mole of NH_4OH and 0.045 mole of $(\text{NH}_4)_2\text{CO}_3$ was treated with a solution of 0.91 mole of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.09 mole of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at a temperature of about 60°C ($\text{pH} = 9$). After filtration, washing and drying at about 100°C for about 15 hours, a hydrotalcite $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ was formed. The material thus obtained was calcined at 700°C for about 15 hours, whereby Mg(Al)O was formed. The structure was confirmed by X-ray diffraction analysis, and the surface area was measured to be $176 \text{ m}^2/\text{g}$.

Example 2

A Mg(Al)O material having an atomic ratio of Mg to Al of 3:1 was prepared according to the following procedure: An aqueous solution of NaOH and Na_2CO_3 was treated with a solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in a similar way as in example 1 resulting in the above mentioned Mg(Al)O material. After filtration, washing and drying also in a similar way as in example 1 a hydrotalcite $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ was formed. The structure was confirmed by X-ray diffraction analysis.

- a) The material thus obtained was calcined at about 700°C for about 15 hours, whereby Mg(Al)O was formed. The structure was confirmed by X-ray diffraction analysis, and the surface area was measured to be $187 \text{ m}^2/\text{g}$.
- b) The material thus obtained was calcined at about 800°C for about 15 hours, whereby Mg(Al)O was formed. The structure was confirmed by X-ray diffraction analysis, and the surface area was measured to be $162 \text{ m}^2/\text{g}$.
- c) The material thus obtained was calcined at about 900°C for about 15 hours, whereby Mg(Al)O was formed, together with traces of inverse MgAl_2O_4 spinel. The structure was confirmed by X-ray diffraction analysis, and the surface area was measured to be $110 \text{ m}^2/\text{g}$.
- d) The material thus obtained was calcined at about 1000°C for about 15 hours, whereby Mg(Al)O was formed, together with some inverse MgAl_2O_4 spinel. The

structure was confirmed by X-ray diffraction analysis, and the surface area was measured to be 61 m²/g.

Example 3

A Mg(Al)O material having an atomic ratio of Mg to Al of 5:1 was prepared according to the following procedure: An aqueous solution of NaOH and Na₂CO₃ was treated with a solution of MgCl₂·6H₂O and AlCl₃·6H₂O in a similar way as in example 1 resulting in the above mentioned Mg(Al)O material. After filtration, washing and drying also in a similar way as in example 1 a hydrotalcite Mg₅Al₂(OH)₁₆CO₃·4H₂O was formed. The structure was confirmed by X-ray diffraction analysis.

- a) The material thus obtained was calcined at about 700°C for about 15 hours, whereby Mg(Al)O was formed. The structure was confirmed by X-ray diffraction analysis, and the surface area was measured to be 169 m²/g.
- b) The material thus obtained was calcined at about 800°C for about 15 hours, whereby Mg(Al)O was formed. The structure was confirmed by X-ray diffraction analysis, and the surface area was measured to be 157 m²/g.

Example 4

To investigate their steam stability, the support materials obtained as described in Examples 1, 2a) and 3a) were tested in a fluidized bed quartz apparatus. The steam stability test procedure was as follows:

The material was loaded into the reactor, which was then heated to 600°C under a N₂ flow. When 600°C was reached, steam was added to the feed. Such conditions (600°C, 50%H₂O/50%N₂) were maintained for 22 hours. A sample of the material was then withdrawn from the reactor, and the temperature increased to 650°C. Such conditions (650°C, 50%H₂O/50%N₂) were maintained for 48 hours. New samples were withdrawn at 650°C. After completion of the test, the steam feed was turned off, and the reactor cooled to 25°C under a N₂ flow. The remainder of

the material was then collected. The sample materials were analysed by BET and XRD.

The steam stability test results are shown in Figure 1 and 3. (Example 1 is only included in Figure 3). The surface area in m^2/g plotted along the vertical axis is expressed as a function of the duration of the steam stability test in hours (plotted along the horizontal axis).

Example 5

To investigate the influence of calcination temperature on the materials' steam stability, the support materials obtained as described in Examples 2b) and 3b) were tested in a fluidized bed quartz apparatus, according to Example 4, but with a prolonged test duration at 650°C (336 hours).

The results for the whole test (314 hours) are shown in Figure 2. The test for the first 72 hours is shown in Figure 1 together with the results from Example 4. The surface area in m^2/g plotted along the vertical axis is expressed as a function of the duration of the steam stability test in hours (plotted along the horizontal axis).

Example 6

To investigate its thermal stability, the support material obtained as described in Example 3b was tested as described in Example 5, except that 100% N_2 was used as feed gas during the whole test. The thermal stability test results are shown in Figure 4.

Example 7

A $\text{Mg}(\text{Al})\text{O}$ material having a particle size less than $100\ \mu\text{m}$, prepared according to any one of Example 1-3, was impregnated with a solution containing tin chloride and hexachloroplatinic acid according to the following procedure:

0.2304 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.0805 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were dissolved in 80 ml of ethanol and the mixture was added to 10.1 g of $\text{Mg}(\text{Al})\text{O}$. After completion of the impregnation the material thus obtained was evaporated to dryness in a vacuum

and was then dried at about 100°C for about 15 hours, whereupon the dried material was calcined at 560°C for about 3 hours in air supplied in an amount of 100 cm³/min.

Example 8

To investigate its steam stability, a material prepared as described in Example 7, with Mg/Al ratio of 3, and which had been calcined at 700°C prior to impregnation, was tested as described in Example 4. The steam stability test results are shown in Figure 1.

Example 9

To investigate its stability during catalytic testing, two materials prepared as described in Example 7, with a Mg/Al ratio of 3, and which had been calcined at 700 or 800°C prior to impregnation, were pelletised by pressing, crushing and sieving to a pellet size of 0.7-1.0 mm, and tested as a catalyst for propane dehydrogenation. The tests were performed in a titanium laboratory scale fixed bed reactor with an inner diameter of 9 mm. A titanium tube with an outer diameter of 3 mm was located in the center of the reactor. The catalyst pellets were placed on a titanium sinter in the reactor. The reactor temperature was controlled by a thermocouple placed in the tube inside the reactor. The total pressure in the reactor was 1.1 bar. The catalysts (appx. 1 g) were tested under the following conditions: T = 600-620°C, GHSV = 600 h⁻¹ and C₃H₈:H₂O = 1:2 (mole basis). The BET surface area measured before and after testing is shown in Table 1.

Table 1: Catalytic testing.

Calcination temperature (°C)	Test duration (h)	BET surface area (m ² /g), after:	
		Pelletisation	Testing
700	380	124	112
800	380	131	121

The results presented in the Examples show that the initial surface area of the calcined materials decreases with increasing calcination temperature. The results presented in Figure 1 and 2 further show that the materials calcined at a higher temperature maintain a higher specific surface area during subsequent steam testing at 600-650°C. Indeed, for a steam test duration of more than 72 hours, the materials calcined at 800°C have a higher specific surface area than those calcined at 700°C.

It is further observed that the initial specific surface area of the materials calcined at a certain temperature, decreases with an increasing Mg/Al ratio. During subsequent steam testing for 336 hours the material with a higher Mg/Al ratio maintain a higher specific surface area compared to the material with a lower Mg/Al ratio (Figure 2). Indeed, after 50 hours of steam testing, the order of specific surface area is reversed, so that the materials with a higher Mg/Al ratio have a higher specific surface area than those with a lower Mg/Al ratio (Figure 1).

Preparation of the material with NH_4^+ instead of Na^+ precursor led to a material with a slightly lower initial specific surface area but with a higher stability during steam testing (Figure 3).

Impregnation of a calcined material with Pt and Sn led to a decrease in the initial specific surface area of that material. The subsequent decrease in specific surface

area during steam testing was similar to that observed for the fresh material (Figure 1).

Pelletisation of the impregnated materials led to a decrease in their specific surface area (Table 1). Subsequent testing of the material as a propane dehydrogenation catalyst showed that the excellent surface area stability observed for these materials during steam testing, is also valid under catalytic test conditions. Even here, an improved stability was indicated for the material calcined at 800°C.

Finally, it is observed that the presence of steam is an important factor for the thermal stability of the materials covered by this invention: When no steam was added to the feed the specific surface area of a Mg/Al = 5 material calcined at 800°C was stable throughout a 334 hours test at 600-650°C (Figure 4).

This means that to prevent sintering of the catalyst support during the dehydrogenation of alkanes, the dehydrogenation can advantageously be performed without steam.

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Patent claims

1. Catalyst support material comprising a mixed oxide consisting essentially of a divalent metal and a trivalent metal in a substantially homogeneous phase, which is a calcination product of a hydrotalcite-like phase calcinated at a temperature of about 700 - 1200 °C, wherein the divalent metal/trivalent metal molar ratio is equal to, or higher than 2.
2. The catalyst support material of the claim 1, wherein the divalent metal is Mg and the trivalent metal is Al.
3. The catalyst support material of the claim 2, which is a calcination product of a hydrotalcite(-like) phase calcinated at a temperature of about 750 - 950 °C.
4. The catalyst support material of claim 1 - 3, wherein the hydrotalcite(-like) phase has been calcinated at a temperature of about 770 - 850 °C .
5. The catalyst support material of claim 1 - 4, wherein the hydrotalcite(-like) phase has been calcinated at a temperature of about 800 °C .
6. The catalyst support material according to claim 2 - 5, wherein the Mg/Al molar ratio is in the range about 2,5 to about 6,0.
7. The catalyst support material according to claim 4, wherein the Mg/Al molar ratio is in the range about 3 to about 5.
8. A method for preparing the catalyst support material according to claim 1, wherein a solution comprising a divalent metal salt and a trivalent metal salt is mixed with a basic aqueous solution, the reaction product recovered from said reaction mixture, said product being washed and dried, and the dried product calcinated at a temperature ranging from 700 - 1200 °C.

9. The method of the claim 8, wherein the divalent metal is Mg and the trivalent metal is Al.
10. The method of the claims 8 and 9, wherein the hydrotalcite(-like) phase is calcinated at a temperature of about 750 - 950 °C.
11. The method of the claims 8 - 10, wherein the dried product is calcinated at a temperature ranging from about 770 to about 850 °C.
12. The method of the claims 8 - 11, wherein the dried product is calcinated at a temperature about 800 °C.
13. The method of the claims 8 to 12, wherein the basic aqueous solution is a composition of aqueous ammonium or alkali metal hydroxides and carbonates.
14. The process of the claim 13, wherein the basic aqueous solution is a composition of aqueous ammonium hydroxides and carbonates.
15. A dehydrogenation catalyst comprising a 1. Transition row metal of the Periodic System and/or a Group VIII metal impregnated onto the catalyst support material according to the claims 1 - 7.
16. The dehydrogenation catalyst of the claim 15, wherein the 1. Transition row metal of the Periodic System is Cr.
17. The catalyst according to the claims 15 and 16, wherein a Group IVA metal and optionally a Group IA metal have been impregnated together with a Group VIII metal onto the catalyst support material according to claim 1.
18. The catalyst according to any one of claims 15 - 17, wherein the Group VIII metal is Pt, and the Group IVA metal is Sn, and the Group IA metal is Cs.

19. The catalyst according to any one of claims 15 - 18, wherein the amount of the Group VIII metal is 0.05-5.0 % by weight, the amount of the Group IVA metal is 0.05-7.0 % by weight, and the amount of the optional Group IA metal is 0.05 - 5.0 % by weight.
20. A process for the catalytic dehydrogenation of light alkanes, wherein a stream of light alkanes are passed through a layer of the catalytically active compositions according to any one of claims 15 - 19 in the presence or absence of steam.
21. The process of the claim 20, wherein the catalytic dehydrogenation is performed in the presence of steam.
22. The process of claim 20, wherein the catalytic dehydrogenation is performed in the absence of steam.
23. The use of a catalytic composition according to any of the claims 15 - 19 for the dehydrogenation of light alkanes.

1/4

Figure 1: Steam stabilisation tests at 650 degrees celcius, Materials prepared by Mg/Al ratio 3 and 5 and calcination temperature 700 and 800 degrees celcius

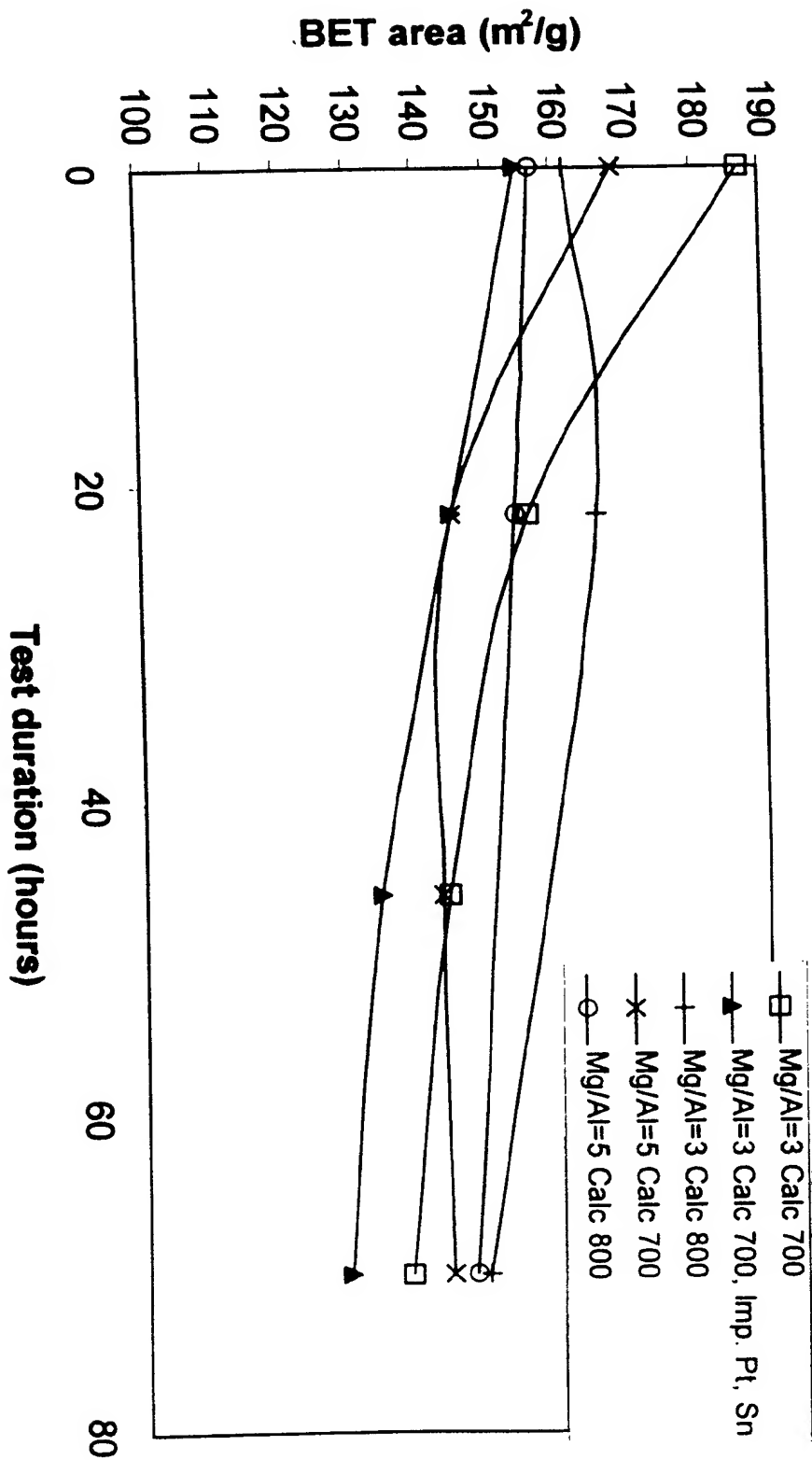
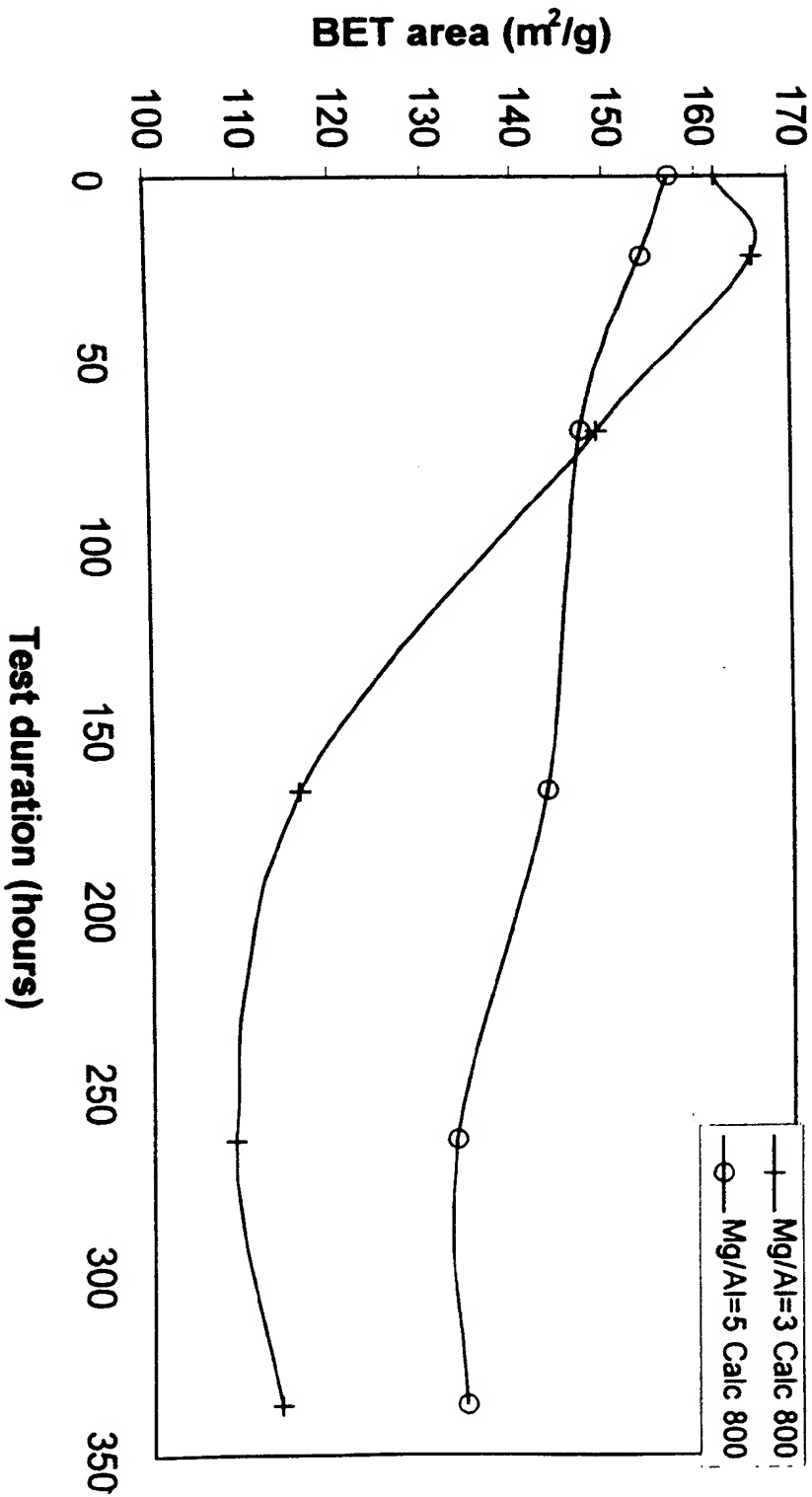
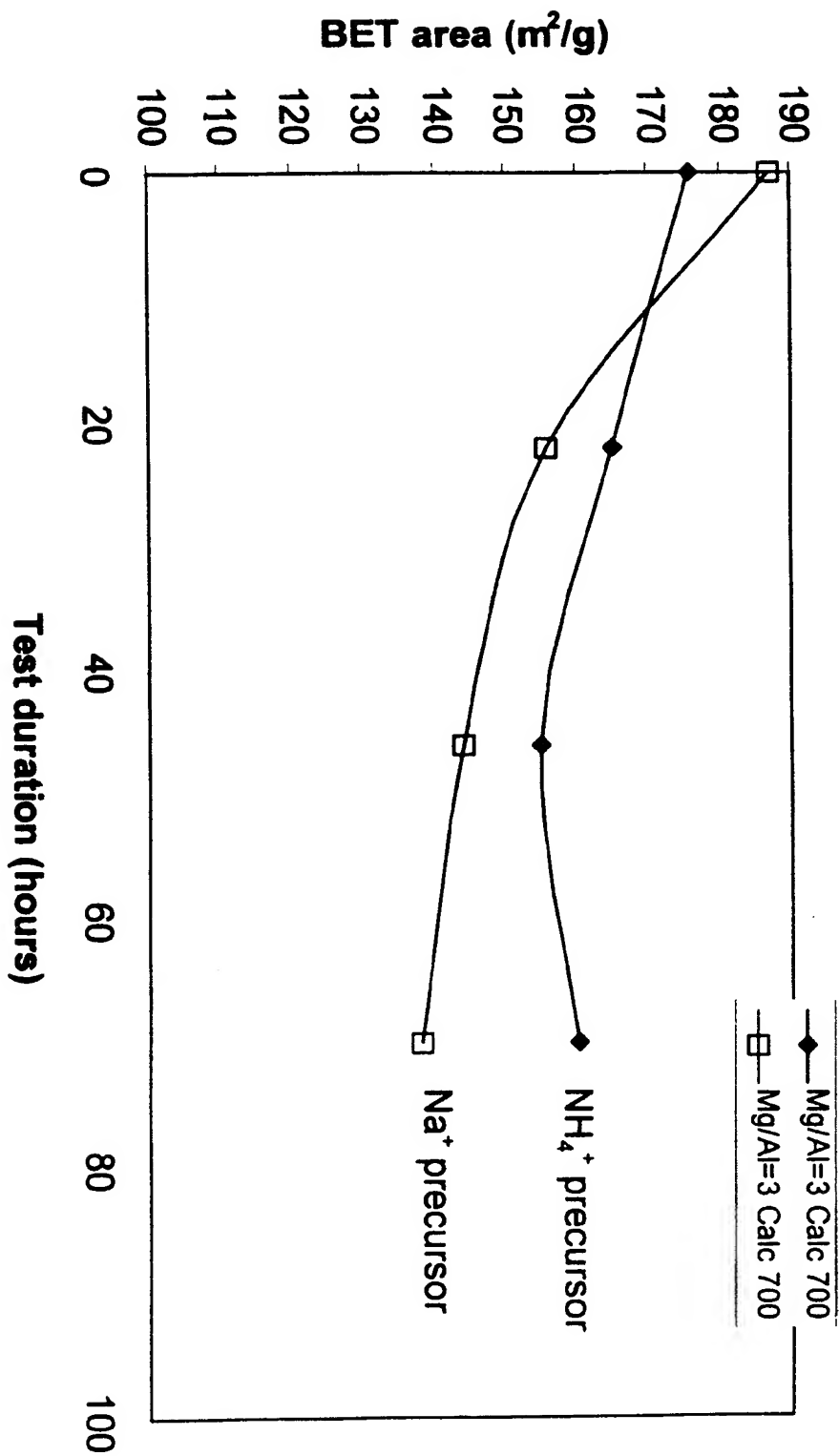


Figure 2: Steam stabilisation tests at 650 degrees celcius, Materials prepared by Mg/Al ratio 3 and 5 and calcination temperature 800 degrees celcius



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Figure 3: Steam stabilisation tests at 650 degrees celcius, Materials prepared from ammonium- and sodium ions solutions, Mg/Al = 3 and calcination temperature 700 degrees celcius



4/4

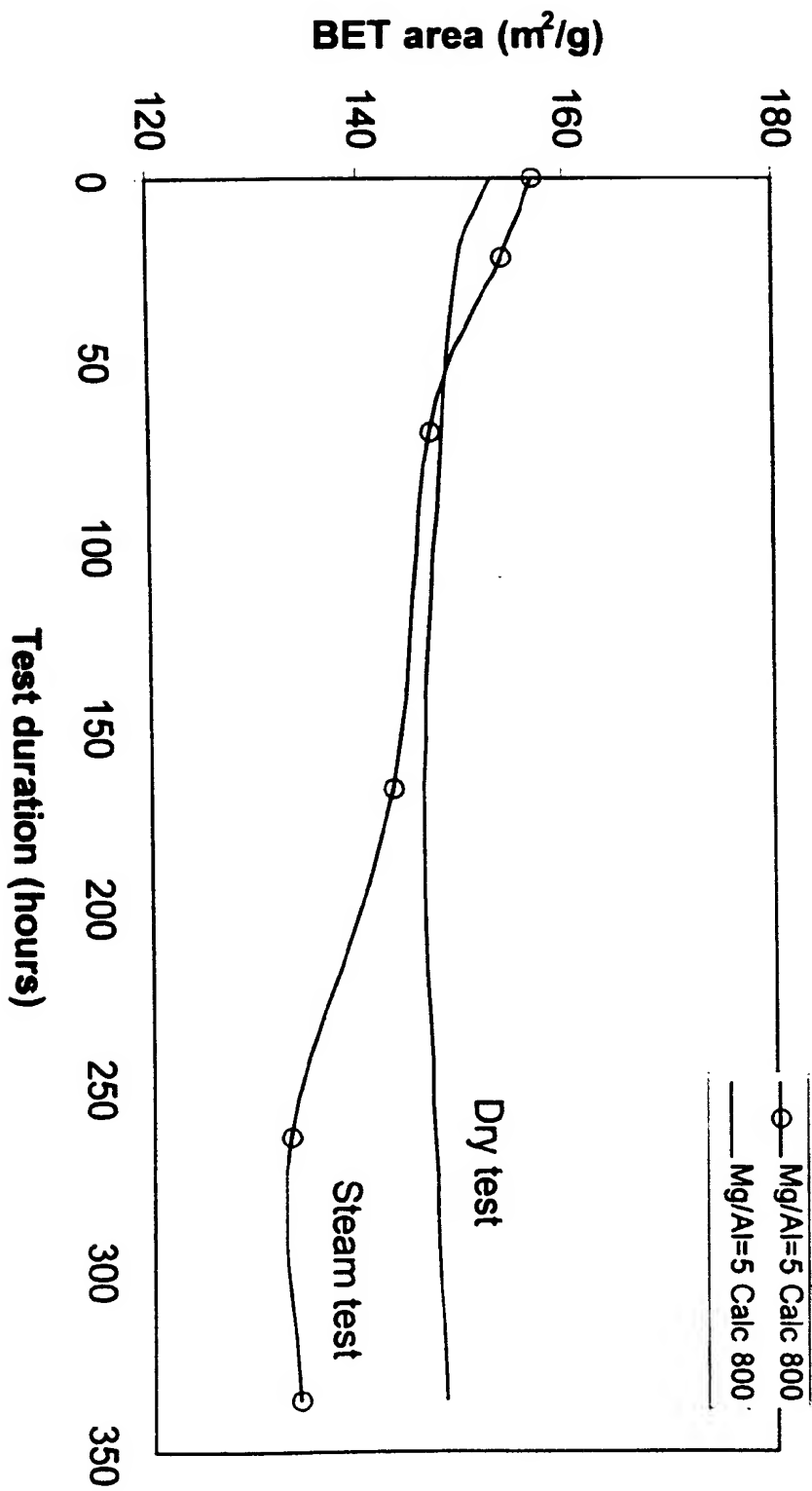


Figure 4: Steam stabilisation test and thermic stabilisation test at 650 degrees celcius, Materials prepared by Mg/Al = 5 and calcination temperature 800 degrees celcius

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00085

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 21/10, B01J 23/62, B01J 23/58, C07C 5/333
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9429021 A1 (DEN NORSKE STATS OLJESELSKAP A.S.), 22 December 1994 (22.12.94), page 3, line 25 - line 28; page 7, line 27 - column 9, line 24, claims 1-22 --	1-2,4,6-9, 13-15,17-21, 23
X	EP 0251351 A2 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.), 7 January 1988 (07.01.88), claims 1-9, abstract --	1-2,8-9
A	WO 9623727 A1 (RWEDEA AKTIENGESELLSCHAFT FÜR MINERALOEL UND CHEMIE), 8 August 1996 (08.08.96) --	1-23

☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search	Date of mailing of the international search report
16 June 1999	03 -07- 1999
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Britt-Marie Lundell/MP Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 99/00085

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5439861 A (ALAKANANDA BHATTACHARYYA ET AL), 8 August 1995 (08.08.95) -- -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/06/99

International application No.

PCT/NO 99/00085

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WO 9429021 A1	22/12/94	AT 177971 T AU 7009094 A DE 69417416 D EP 0705136 A,B NO 179131 B,C NO 932173 A NO 954943 A US 5817596 A	15/04/99 03/01/95 00/00/00 10/04/96 06/05/96 15/12/94 06/12/95 06/10/98
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WO 9623727 A1	08/08/96	DE 19503522 A EP 0807086 A JP 10513145 T	08/08/96 19/11/97 15/12/98
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